

DECLARATION



I, Atsuko Ikeda, residing at 26-2-906, Ojima 3-chome, Koto-ku, Tokyo, Japan, do hereby certify that I am conversant with the English and Japanese languages and am a competent translator thereof. I further certify that to the best of my knowledge and belief the attached English translation is a true and correct translation made by me of U.S. Provisional Patent Application No. 60/192,880 filed on March 29, 2000.

I further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code and that such willful false statements may jeopardize the validity of the application or any patent issuing thereon.

Signed this 27th day of July, 2000


Atsuko Ikeda

RECEIVED
SEP 19 2000
JC 1700 MAIL ROOM

[NAME OF DOCUMENT] Specification

[TITLE OF THE INVENTION]

Method for Manufacturing Ester

[SCOPE OF CLAIM FOR PATENT]

[Claim 1] A method for manufacturing an ester, comprising manufacturing an ester from a carboxylic acid and an ethylene in the presence of an acid catalyst, wherein the concentration of an olefin having 3 or more carbon atoms in the starting materials is 10,000 ppm or less in terms of the molar ratio to the total of said substance and the ethylene.

[Claim 2] The method for manufacturing an ester as claimed in claim 1, wherein the concentration of an olefin having 3 or more carbon atoms in the starting materials is 5,000 ppm or less in terms of the molar ratio to the total of said substance and the ethylene.

[Claim 3] The method for manufacturing an ester as claimed in claim 1 or 2, wherein the concentration of an olefin having 3 or more carbon atoms in the starting materials is 1,000 ppm or less in terms of the molar ratio to the total of said substance and the ethylene.

[Claim 4] The method for manufacturing an ester as claimed in any one of claims 1 to 3, wherein the olefin having 3 or more carbon atoms contains at least one compound selected from the group consisting of trans-2-

butene, cis-2-butene and 1-butene.

[Claim 5] A method for manufacturing an ester, comprising manufacturing an ester from a carboxylic acid and an ethylene in the presence of an acid catalyst, wherein the concentration of an equivalent of an olefin in the starting materials is 50,000 ppm or less in terms of the molar ratio to the total of said substance and the ethylene.

[Claim 6] The method for manufacturing an ester as claimed in claim 5, wherein the concentration of an equivalent of an olefin in the starting materials is 25,000 ppm or less in terms of the molar ratio to the total of said substance and the ethylene.

[Claim 7] The method for manufacturing an ester as claimed in any one of claims 5 to 6, wherein the concentration of an equivalent of an olefin in the starting materials is 5,000 ppm or less in terms of the molar ratio to the total of said substance and the ethylene.

[Claim 8] The method for manufacturing an ester as claimed in any one of claims 5 to 7, wherein the equivalent of an olefin contains at least one compound selected from the group consisting of a saturated alcohol having 3 or more carbon atoms, an ester consisting of a carboxylic acid and a saturated alcohol having 3 or more carbon atoms, and a saturated ether having 5 or more carbon atoms.

[Claim 9] A method for manufacturing an ester, comprising manufacturing an ester from a carboxylic acid and an ethylene in the presence of an acid catalyst, wherein the sum of the concentration of an olefin having 3 or more carbon atoms and one-fifth the concentration of an equivalent of an olefin in the starting materials is 10,000 ppm or less in terms of the molar ratio to the total of said substances and the ethylene.

[Claim 10] The method for manufacturing an ester as claimed in claim 9, wherein the sum of the concentration of an olefin having 3 or more carbon atoms and one-fifth the concentration of an equivalent of an olefin in the starting materials is 5,000 ppm or less in terms of the molar ratio to the total of said substances and the ethylene.

[Claim 11] The method for manufacturing an ester as claimed in any one of claim 9 or 10, wherein the sum of the concentration of an olefin having 3 or more carbon atoms and one-fifth the concentration of an equivalent of an olefin in the starting materials is 1,000 ppm or less in terms of the molar ratio to the total of said substances and the ethylene.

[Claim 12] The method for manufacturing an ester as claimed in any one of claims 9 to 11, wherein the olefin having 3 or more carbon atoms contains at least one compound selected from the group consisting of trans-2-

butene, cis-2-butene and 1-butene.

[Claim 13] The method for manufacturing an ester as claimed in any one of claims 9 to 11, wherein the equivalent of an olefin contains at least one compound selected from the group consisting of a saturated alcohol having 3 or more carbon atoms, an ester consisting of a carboxylic acid and a saturated alcohol having 3 or more carbon atoms, and a saturated ether having 5 or more carbon atoms.

[Claim 14] The method for manufacturing an ester as claimed in any one of claims 1 to 13, comprising manufacturing an ester from a carboxylic acid and an ethylene in the presence of an acid catalyst, wherein said method is performed in the presence of water.

[Claim 15] The method for manufacturing an ester as claimed in any one of claims 1 to 14, wherein the carboxylic acid is one or more of lower aliphatic carboxylic acids having from 1 to 4 carbon atoms.

[Claim 16] The method for manufacturing an ester as claimed in any one of claims 1 to 14, wherein the acid catalyst contains at least one compound selected from a heteropolyacid and/or a heteropolyacid salt.

[Claim 17] The method for manufacturing an ester as claimed in claim 16, wherein the heteropolyacid contains at least one compound selected from the group consisting of a

silicotungstic acid, a phosphotungstic acid, a phosphomolybdic acid, a silicomolybdic acid, a silicovanadotungstic acid, a phosphovanadotungstic acid and a phosphovanadomolybdic acid.

[Claim 18] The method for manufacturing an ester as claimed in claim 16, wherein the heteropolyacid salt contains at least one compound selected from the group consisting of a lithium salt, a sodium salt, a potassium salt, a cesium salt, a magnesium salt, a barium salt, a copper salt, a gold salt, a gallium salt and an ammonium salt.

[DETAILED DESCRIPTION OF THE INVENTION]

[0001]

[Technical Field to Which the Invention Belongs]

The present invention relates to a method for manufacturing an ester by reacting an ethylene and a carboxylic acid.

[0002]

[Background Art]

As is well known, a lower olefin and a lower aliphatic carboxylic acid are reacted in the presence of an acid catalyst to obtain the corresponding ester. Also, in this reaction, a heteropolyacid and/or heteropolyacid salt is known to effectively act as a catalyst. Specific examples of these conventional techniques include those

described, for example, in JP-A-4-139148 (the term "JP-A" as used herein means an "unexamined published Japanese patent application"), JP-A-4-139149, JP-A-5-65248, JP-A-5-163200, JP-A-5-170699, JP-A-5-255185, JP-A-5-294894, JP-A-6-72951, JP-A-9-118647. Thus, the development of catalysts having high initial activity is proceeding.

[0003]

However, in the industrial production methods, impurities derived from the starting materials or by-products yielded during the reaction cause deterioration of the catalyst and in turn the reaction result disadvantageously decreases. Particularly, in the process having a circulation system, if a reaction is continuously performed for a long time, various impurities or by-products accumulate in the system and due to the effect thereof, for example, a vicious circle arises such that the catalyst deteriorates and the side reaction is further accelerated.

[0004]

[Problems to be Solved by the Invention]

The object of the present invention is to provide a method for manufacturing an ester by esterifying a carboxylic acid with an ethylene in a vapor phase, where the operation can be continuously and stably performed for a long period of time.

[0005]

In particular, the object of the present invention is to provide the above-described method for manufacturing an ester, where in the process having a circulation system, the impurities derived from the starting materials or the compounds derived from the by-products produced by a side reaction are reduced to a low concentration based on the starting materials, so that the catalyst can be prevented from deteriorating and in turn the operation can be continuously and stably performed for a long period of time.

[0006]

[Means to Solve the Problems]

The present inventors have made extensive studies to investigate a method for manufacturing an ester by reacting an ethylene and a carboxylic acid, in which deterioration of the catalyst is hard to occur and the operation can be continuously and stably performed for a long period of time.

[0007]

As a result, it has been found that in a method for manufacturing an ester by esterifying a carboxylic acid and an ethylene using an acid catalyst in a vapor phase, when the concentration of an olefin having 3 or more carbon atoms in the starting materials is controlled to 10,000 ppm or less in terms of the molar ratio to the total of this substance and the ethylene, the deterioration of the

catalyst can be remarkably prevented from proceeding and in turn, a continuous and stable operation can be performed for a long time.

[0008]

It has also been found that in the method for manufacturing an ester by esterifying a carboxylic acid and an ethylene using an acid catalyst in a vapor phase, when the concentration of an equivalent of an olefin in the starting materials is controlled to 50,000 ppm or less in terms of the molar ratio to the total of this substance and the ethylene, similarly to the above, the deterioration of the catalyst can be remarkably prevented from proceeding and a continuous and stable operation can be performed for a long time.

[0009]

The present invention is described in detail below.

The term "an olefin having 3 or more carbon atoms" as used in the present invention means olefins at large except for ethylene. Specific examples thereof include linear terminal olefins having 3 or more carbon atoms, such as propylene, 1-butene, 2-butene, isobutene, 1-hexene and 2-octene, internal olefins, branched terminal olefins, branched internal olefins, and cyclic olefins having 3 or more carbon atoms, such as cyclopentane and cyclohexene.

[0010]

Among these, so-called ethylene oligomers derived from an ethylene and produced by the side reaction which may occur under the esterification reaction conditions, such as 1-butene, cis-2-butene, trans-2-butene, 2-methyl-2-pentene and 3-methyl-2-pentene, have a possibility of causing a problem. Of course, the olefins are not limited thereto.

[0011]

The term "an equivalent of an olefin" as used in the present invention means a group of compounds which can produce an olefin having 3 or more carbon atoms under the esterification reaction conditions. Specific examples thereof include hydrates of an olefin having 3 or more carbon atoms, ether compounds produced by the reaction of the hydrate with an ethylene or an olefins having 3 or more carbon atoms, and carboxylic acid esters produced by the reaction of a carboxylic acid with an olefin having 3 or more carbon atoms. However, the equivalent of an olefin is not limited thereto and any compound is included as long as it is a compound capable of producing an olefin having 3 or more carbon atoms under the esterification reaction conditions.

[0012]

Specific examples of the equivalent of an olefin

include the following compounds.

[0013]

Examples of the hydrate of an olefin having 3 or more carbon atoms include isopropanol, n-butyl alcohol, sec-butyl alcohol, t-butyl alcohol and 2-hexanol.

[0014]

Examples of the ether compound produced by the reaction of a hydrate of an olefin having 3 or more carbon atoms with an ethylene or an olefin having 3 or more carbon atoms include ethyl isopropyl ether, ethyl sec-butyl ether, ethyl t-butyl ether, di-sec-butyl ether, di-n-butyl ether and ethyl cyclohexyl ether.

[0015]

Examples of the carboxylic acid ester produced by the reaction of a carboxylic acid with an olefin having 3 or more carbon atoms include isopropyl acetate, sec-butyl acetate, sec-butyl propionate, t-butyl acetate and cyclohexyl acetate.

[0016]

These compounds, namely, hydrates of an olefin, ether compounds and carboxylic acid esters, are the specific examples of the equivalent of an olefin. However, needless to say, the specific examples of the equivalent of an olefin is not limited thereto.

[0017]

The equivalent of an olefin also includes those produced in the reaction system, to say nothing of those contained in the starting materials newly fed to the reaction system.

[0018]

Particularly, in performing the method for producing an ester by the esterification reaction of a carboxylic acid and an ethylene using an acid catalyst in a vapor phase, when water is present in the system, there is a fear that a hydrate is produced by the hydration of an ethylene and also an ether compound or a carboxylic acid ester is further produced from the hydrate. Furthermore, when a circulation system for the unreacted raw materials is integrated into the production process of an ester so as to improve the yield or the like, these hydrate, ether compound and carboxylic acid ester produced in the reaction system may disadvantageously mingle with the unreacted starting materials. In this meaning, "the equivalent of an olefin" as used herein includes these hydrates, ether compounds and carboxylic acid esters produced in the reaction system by the esterification reaction.

[0019]

In the manufacturing method of an ester of the present invention, the concentration of an olefin having 3

or more carbon atoms in the starting materials is controlled to 10,000 ppm or less in terms of the molar ratio to the total of this substance and the ethylene, which is effective in reducing the deterioration rate of the catalyst and in turn continuously and stably performing the operation for a long period of time.

[0020]

The terms "the concentration of an olefin having 3 or more carbon atoms in the starting materials" and "the concentration of an equivalent of an olefin in the starting materials" each means a concentration immediately before the inlet of a reactor for performing the esterification reaction.

[0021]

For example, to speak specifically, in the case where the reaction is performed in the one-path process having no circulation step as shown in Fig. 1, the concentration indicated by (1) immediately before the inlet of a reactor applies. In the process having a circulation step from the post-process as shown in Fig. 2, the concentration indicated by (2) immediately before the inlet of a reactor applies. Needless to say, the present invention is by no means limited to these exemplified processes.

[0022]

Accordingly, the term "starting materials" as used

herein of course include those obtained by recovering unreacted starting materials through a post-process such as separation of the objective compound after the reaction and supplied to the reactor via a circulation system, to say nothing about the ethylene and acetic acid newly fed to the reaction system.

[0023]

The position (1) in the process shown by Fig. 1 and the position (2) in the process shown by Fig. 2 each is kept at a temperature equal to or higher than the reaction temperature in the reactor. Accordingly, for measuring the concentration at such a position, the sampling must be particularly designed.

[0024]

In particular, some equivalents of an olefin are readily condensed when cooled to room temperature, therefore, for avoiding the measurement errors due to the effect thereof, the sampling is necessary to be designed, for example, to separate the condensed components from the non-condensed components by cooling them using an ice trap or the like and analyze respective components.

[0025]

If the concentration of an olefin having 3 or more carbon atoms in the starting materials exceeds 10,000 ppm in terms of the molar ratio to the total of this substance

and the ethylene, the catalytic activity decreases at an extremely high rate, as a result, the catalyst life is greatly shortened. This is considered to occur because the above-described olefin reacts with the ethylene on the catalyst to produce cokes and the active sites of the catalyst are covered by the cokes to cause the deactivation.

[0026]

Accordingly, the concentration of an olefin having 3 or more carbon atoms in the starting materials is preferably as low as possible. These olefins cannot be completely removed with ease, however, the concentration is preferably 5,000 ppm or less, more preferably 1,000 ppm or less.

[0027]

The method for controlling the concentration of an olefin having 3 or more carbon atoms in the starting materials to 10,000 ppm or less in terms of the molar ratio to the total of this substance and the ethylene is not particularly limited. Commonly known separation techniques may be used.

[0028]

As an example, fundamentally, the ethylene used as a starting material is of course refined to reduce the contents of these compounds as much as possible.

[0029]

The olefin having 3 or more carbon atoms produced by the side reaction within the reaction system, which comes to a problem when a circulation system is integrated, can be separated from the ethylene by a method of allowing an appropriate solvent to absorb the main products exclusive of ethylene, the starting materials and the by-products in the reaction gas discharged from the reactor. Also, the raw material gas may be separated from the ethylene by the high-pressure or low-temperature distillation or by using a separation membrane or the like. Other than these specific examples, any method may be used as long as it is a method capable of controlling the concentration of an olefin having 3 or more carbon atoms circulated and guided to the reactor to 10,000 ppm or less in terms of the molar ratio to the total of this substance and the ethylene.

[0030]

If the concentration of the equivalent of an olefin in the starting materials exceeds 50,000 ppm in terms of the molar ratio to the total of this substance and the ethylene, similarly to the case where the concentration of an olefin having 3 or more carbon atoms exceeds 10,000 ppm in terms of the molar ratio to the total of this substance and the ethylene, the catalytic activity decreases at an extremely high rate, as a result, the catalyst life is

greatly shortened.

[0031]

Although it may slightly differ depending on the individual equivalents of an olefin, the equivalent of an olefin generally exhibits an activity of deteriorating the catalyst on the same level as an olefin having 3 or more carbon atoms when the concentration thereof is about 5 times higher. This difference is considered to result from the fact that the equivalent of an olefin produces an olefin after once decomposed on the catalyst and the effect given on the deactivation is low even if the concentration is higher than that of the olefin.

[0032]

However, similarly to an olefin having 3 or more carbon atoms, the concentration is preferably as much as possible. Although complete removal of the equivalent of an olefin may not be attained with ease, the concentration thereof is preferably 25,000 ppm or less, more preferably 5000 ppm or less.

[0033]

The method for controlling the concentration of the equivalent of an olefin in the starting materials to 50,000 ppm or less in terms of a molar ratio to the total of this substance and the ethylene is not particularly limited. Similarly to an olefin having 3 or more carbon atoms,

commonly known separation techniques may be used.

[0034]

When an olefin having 3 or more carbon atoms and an equivalent of an olefin are present together, an interaction therebetween is not particularly observed. Roughly, the sum of one-fifth the concentration of all equivalents of an olefin and the concentration of an olefin having 3 or more carbon atoms in the starting materials is preferably 10,000 ppm or less in terms of the molar ratio to the total of these substances and the ethylene.

[0035]

Needless to say, similarly to their individual concentrations, the concentration here is also preferably low as much as possible and, to speak specifically, it is preferably 5,000 ppm or less, more preferably 1,000 ppm or less.

[0036]

The method for measuring the concentration of an olefin having 3 or more carbon atoms or an equivalent of an olefin is not particularly limited and any method may be used as long as it is a method commonly used for measuring the concentration. Specific examples of the measuring method include a method of placing a cell in a part of the apparatus and spectro-optically measuring the concentration using an appropriate wavelength, and a method of sampling a

part of the starting material and analyzing it by gas chromatography, however, the present invention is by no means limited thereto.

[0037]

The optimal measuring method varies depending on the properties of the object to be measured or the environment in measurement, however, a method which is free of any effect by other components present together, favored with good quantitation and reproduction, small in the measuring threshold value, simple and inexpensive, is preferred.

[0038]

The carboxylic acid for use as a reaction starting material in the present invention is a lower aliphatic carboxylic acid having from 1 to 4 carbon atoms. Preferred are formic acid, acetic acid, acrylic acid, propionic acid and methacrylic acid, and more preferred are acetic acid and acrylic acid.

[0039]

The acid catalyst for use in the present invention is a compound widely used in general as an acid catalyst such as ion-exchange resin, mineral acid, heteropolyacid, zeolite and composite metal oxide. Preferred are a heteropolyacid and a heteropolyacid salt. The heteropolyacid is a compound consisting of a center element and peripheral elements to which oxygen is connected.

[0040]

The center element is usually silicon or phosphorus but not limited thereto and the center element may be any one selected from the elements belonging to Groups 1 to 17 of the Periodic Table. The Periodic Table as used herein indicates the Periodic Table provided in Muki Kagaku Meimeiho, Kaitei-Ban (Nomenclature in Inorganic Chemistry, Revised), Kokusai Junsei Oyobi Oyo Kagaku Rengo (1989).

[0041]

Specific examples of the center element include cupric ion; divalent beryllium, zinc, cobalt and nickel ions; trivalent boron, aluminum, gallium, iron, cerium, arsenic, antimony, phosphorus, bismuth, chromium and rhodium ions; tetravalent silicon, germanium, tin, titanium, zirconium, vanadium, sulfur, tellurium, manganese, nickel, platinum, thorium, hafnium, cerium ions and other rare earth ions; pentavalent phosphorus, arsenic, vanadium and antimony ions; hexavalent tellurium ion; and heptavalent iodide ion, however, the present invention is by no means limited thereto.

[0042]

Specific examples of the peripheral element include tungsten, molybdenum, vanadium, niobium and tantalum, however, the present invention is not limited thereto.

[0043]

These heteropolyacids are also known, e.g., as "polyoxoanion", "polyoxometallate" or "metal oxide cluster". The structures of some of the well known anions are known, for example, as Keggin, Wells-Dawson or Anderson-Evans-Perloff structure. Heteropolyacids usually have a high molecular weight, for example, a molecular weight, e.g., in the range of 700 to 8,500 and includes dimeric complexes.

[0044]

The heteropolyacid salt is not particularly limited as long as it is a metal salt or onium salt resulting from substituting a part or all of the hydrogen atoms of the heteropolyacid.

[0045]

Specific examples thereof include metal salts, e.g., such as lithium, sodium, potassium, cesium, magnesium, barium, copper, gold and gallium, and onium salts such as ammonia, however, the present invention is not limited thereto.

[0046]

Particularly when the heteropolyacid is a free acid or comprises several salts, the heteropolyacid has a relatively high solubility in polar solvents such as water or other oxygenated solvents, and the solubility can be controlled by selecting the appropriate counter ions.

[0047]

Examples of the heteropolyacid which can be particularly preferably used as a catalyst in the present invention include:

Tungstosilicic acid	$H_4[SiW_{12}O_{40}] \cdot xH_2O$
Tungstophosphoric acid	$H_3[PW_{12}O_{40}] \cdot xH_2O$
Molybdophosphoric acid	$H_3[PMo_{12}O_{40}] \cdot xH_2O$
Molybdosilicic acid	$H_4[SiMo_{12}O_{40}] \cdot xH_2O$
Vanadotungstosilicic acid	$H_{4+n}[SiV_nW_{12-n}O_{40}] \cdot xH_2O$
Vanadotungstophosphoric acid	$H_{3+n}[PV_nW_{12-n}O_{40}] \cdot xH_2O$
Vanadomolybdophosphoric acid	$H_{3+n}[PV_nMo_{12-n}O_{40}] \cdot xH_2O$

[0048]

Particularly preferred examples of the heteropolyacid salt include lithium salt, sodium salt, potassium salt, cesium salt, magnesium salt, barium salt, copper salt, gold salt, gallium salt and ammonium salt of the above-described heteropolyacids which are particularly preferred.

[0049]

The acid catalyst may be supported on a support. In this case, the acid catalyst content is preferably from 10 to 200 mass%, more preferably from 50 to 150 mass%, based on the entire mass of the support.

[0050]

If the acid catalyst content is less than 10 mass%, the content of active components in the catalyst is

excessively lower and the activity per the catalyst unit mass may disadvantageously decrease.

[0051]

If the content of the acid catalyst exceeds 200 mass%, the effective surface area decreases, as a result, the effect owing to the increase in the supported amount may not be brought out and at the same time, coking is disadvantageously liable to occur to greatly shorten the catalyst life.

[0052]

The substance which can be used as a support for the acid catalyst of the present invention is not particularly limited and those capable of providing, when prepared as a catalyst by bearing the acid catalyst, a catalyst having a specific surface area by the BET method of from 65 to 350 m²/g are preferred.

[0053]

The shape of the substance which can be used as a support for the catalyst of the present invention is not particularly limited and to speak specifically, powder, sphere, pellet and any other forms may be used. Specific examples thereof include silica, diatomaceous, montmorillonite, titania, activated carbon, alumina and silica alumina, however, the present invention is not limited thereto.

[0054]

The support is preferably a support comprising a siliceous main component and having a spherical or pellet form, more preferably a silica having a purity of 95 mass% or more based on the entire mass of the support.

[0055]

The average diameter thereof is preferably from 2 to 10 mm in case of a fixed bed and from powder to 5 mm in case of a fluid bed, though it varies depending on the reaction form.

[0056]

The acid catalyst for use in the present invention can be produced by any desired method. An example of the method for manufacturing a heteropolyacid and/or heteropolyacid salt catalyst is described below.

First Step:

This is a step for obtaining a solution or suspension of a heteropolyacid and/or a heteropolyacid salt.

Second Step:

This is a step for supporting the solution or suspension obtained in the first step on a support.

[0057]

The solvent which can be used in the first step is not particularly limited as long as it can uniformly dissolve or suspend the desired heteropolyacid and/or

heteropolyacid salt, and water, an organic solvent or a mixture thereof may be used. Preferred examples thereof include water, alcohols and carboxylic acids, however, the present invention is not limited thereto.

[0058]

The method for dissolving or suspending a heteropolyacid and/or a heteropolyacid salt in the solvent is not particularly limited and any method may be used as long as it can uniformly dissolve or suspend a desired desirable heteropolyacid and/or heteropolyacid salt.

[0059]

For example, in the case of a heteropolyacid, namely, a free acid, if it can dissolve, the heteropolyacid may be dissolved as it is. Even when the heteropolyacid cannot completely dissolve, if the heteropolyacid can be uniformly suspended by forming it into fine powder, the heteropolyacid may be suspended as such. In the case of a heteropolyacid salt, a method of dissolving a heteropolyacid and a starting material salt for a neutralizing element together or separately and then mixing them to prepare a uniform solution or suspension may be used. Furthermore, in the case of a compound which is in the state of a heteropolyacid salt, a uniform solution or suspension may be obtained in the same manner as in the heteropolyacid.

[0060]

The optimal volume of the solution or suspension varies depending on the supporting method in the second step and the support used but this is not particularly limited.

[0061]

The second step is a step for supporting a solution or suspension of a heteropolyacid and/or a heteropolyacid salt obtained in the first step on a support to obtain a catalyst for use in the manufacture of a lower aliphatic ester.

[0062]

The method for bearing the solution or suspension of a heteropolyacid and/or a heteropolyacid salt on a support is not particularly limited and a known method may be used.

[0063]

For example, the catalyst may be prepared by dissolving or suspending a heteropolyacid and/or a heteropolyacid salt in a solvent so as to form a solution or suspension corresponding to the liquid absorption amount of the support and impregnating the solution or suspension into a support.

[0064]

The catalyst may also be prepared by using an excess solution or suspension, impregnating it into a support

while moderately moving the support in the solution or suspension of a heteropolyacid and/or a heteropolyacid salt and then removing the excess acid through filtration.

[0065]

The wet catalyst obtained as such is preferably dried by placing it in a heating oven for a few hours. Thereafter, the catalyst is cooled to the ambient temperature in a desiccator. The drying temperature is not particularly limited but if it exceeds about 400°C, the skeleton of the heteropolyacid may be disadvantageously destroyed. The drying temperature is preferably from 80 to 350°C.

[0066]

Industrially, the catalyst may be continuously dried using a dryer such as through-flow rotary dryer, continuous fluidized bed dryer or continuous hot air carrier type dryer.

[0067]

The amount of the heteropolyacid and/or heteropolyacid salt supported can be calculated simply by subtracting the mass of the support used from the dry mass of the catalyst prepared. A more exact amount may be measured by chemical analysis such as ICP (inductively coupled plasma emission spectrometry).

[0068]

In practicing the manufacturing method of an ester of the present invention, the ratio between the ethylene and the carboxylic acid used is preferably such that the ethylene is used in an equimolar amount or excess molar amount to the carboxylic acid. The ratio of ethylene : carboxylic acid is preferably, as a molar ratio, from 1:1 to 30:1, more preferably from 3:1 to 20:1, still more preferably from 5:1 to 15:1.

[0069]

In the manufacturing method of an ester of the present invention, the vapor phase reaction may be performed in either a fixed bed form or a fluidized bed form. The shape of the support may also be selected from those formed into a size of from powder to a few mm according to the form of the practice.

[0070]

In the manufacturing method of an ester of the present invention, a slight amount of water is preferably mixed in the starting materials from the standpoint of the catalyst life. However, if an excessively large amount of water is added, by-products such as alcohol and ether disadvantageously increase. In general, the amount of water is preferably from 1 to 15 mol%, more preferably from 2 to 8 mol%, in the entire amount of the olefin and

carboxylic acid used.

[0071]

The reaction temperature and pressure must be in the range capable of keeping the supply medium in a gaseous form and vary depending on the starting materials used. In general, the reaction temperature is preferably from 120 to 250°C, more preferably from 140 to 220°C.

[0072]

The pressure is preferably from atmospheric pressure to 3 MPa, more preferably from atmospheric pressure to 2 MPa.

[0073]

With respect to the space velocity (GHSV) of the raw materials, these are preferably passed through the catalyst layer at a GHSV of from 100 to 7,000/hr, more preferably from 300 to 3,000/hr.

[0074]

[0075]

The present invention is described in greater detail below by referring to the Examples and Reference Example, however, these Examples are only for describing the outline of the present invention, and the present invention should not be construed as being limited thereto.

[0076]

[Examples]

<Analysis of Reaction Gas>

In Examples 1 to 12 and Comparative Examples 1 to 7 which are examples of the one-path process having no recycle system, the starting material composition fed to the reactor was used as the inlet gas concentration.

[0077]

In Examples 13 to 15 and Comparative Example 8 which are examples of the process having a recycle system, for a gas at the inlet of the reactor, when a predetermined time was passed after the initiation of the reaction, a part of the gas was sampled by a three-way valve and cooled and the concentrated solution collected was recovered in the whole amount and analyzed by gas chromatography. With respect to the effluent gas remaining uncondensed, the flow rate of the gas at the outlet discharged within the sampling time was measured and a part of the gas was sampled and analyzed on the composition by gas chromatography. On the other hand, for a gas at the outlet, the whole amount of the gas was cooled and the concentrated reaction solution collected was recovered in the whole amount and analyzed by gas chromatography. With respect to the effluent gas remaining uncondensed, the flow rate of the gas at the outlet discharged within the sampling time was measured and a part

of the gas was sampled and analyzed on the composition by gas chromatography. The analysis conditions are shown below.

[0078]

Conditions for Analysis of Uncondensed Gas

An absolute calibration curve method was used for the analysis. The analysis was performed under the following conditions by sampling 50 ml of the effluent gas and allowing the whole amount thereof to flow into a 1 ml-volume gas sampler attached to the gas chromatograph.

[0079]

1. Ether, Carboxylic Acid Ester, Alcohol, Trace By-Products

Gas chromatography:

gas chromatograph (GC-14B, manufactured by Shimadzu Corporation) with a gas sampler (MGS-4, measuring tube: 1 ml) for Shimadzu gas chromatograph

Column:

packed column SPAN80 15% Shinchrom A, 60 to 80 mesh
(length: 5 m)

Carrier gas:

nitrogen (flow rate: 25 ml/min)

Temperature conditions:

constant temperature conditions that the detector and the vaporization chamber were at 120°C and the column was at 65°C

Detector:

FID (H₂ pressure: 60 kPa, air pressure: 100 kPa)

[0080]

2. Butene

Gas chromatography:

gas chromatograph (GC-14B, manufactured by Shimadzu Corporation) with a gas sampler (MGS-4, measuring tube: 1 ml) for Shimadzu gas chromatograph

Column:

packed column Unicarbon A-400, length: 2 m

Carrier gas:

helium (flow rate: 23 ml/min)

Temperature conditions:

the temperatures of the detector and the vaporization chamber were 120°C and the column temperature was elevated from 40°C to 95°C at a temperature rising rate of 40°C/min

Detector:

FID (H₂ pressure: 70 kPa, air pressure: 100 kPa)

[0081]

3. Ethylene

Gas chromatography:

gas chromatograph (GC-14B, manufactured by Shimadzu Corporation) with a gas sampler (MGS-4, measuring tube: 1 ml) for Shimadzu gas chromatograph

Column:

packed column Unibeads 1S, length: 3 m

Carrier gas:

helium (flow rate: 20 ml/min)

Temperature conditions:

constant temperature conditions that the detector and the vaporization chamber were at 120°C and the column was at 65°C

Detector:

TCD (He pressure: 70 kPa, current: 90 mA, temperature: 120°C)

[0082]

Analysis of Collected Solution

The analysis was performed using the internal standard method, where the analysis solution was prepared by adding 1 ml of 1,4-dioxane as the internal standard to 10 ml of the reaction solution and 0.4 µl of the analysis solution was injected.

Gas chromatography:

GC-14B, manufactured by Shimadzu Corporation

Column:

capillary column TC-WAX (length: 30 m, internal diameter: 0.25 mm, film thickness: 0.25 µm)

Carrier gas:

nitrogen (split ratio: 20, column flow rate: 2

ml/min)

Temperature conditions:

the temperatures of the detector and the vaporization chamber were 200°C and the column was kept at 50°C for 5 minutes from the initiation of the analysis, thereafter elevated up to 150°C at a temperature rising rate of 20°C/min, and kept at 150°C for 10 minutes

Detector:

FID (H₂ pressure: 70 kPa, air pressure: 100 kPa)

[0083]

<Support>

Support 1:

natural silica (KA-0, produced by SUD-CHEMIE AG)
(specific surface area: 68.5 m²/g, pore volume: 0.71 cm³/g)

Support 2:

synthetic silica (CARIACT Q-10, produced by Fuji Silicia Kagaku K.K.) (specific surface area: 219.8 m²/g, pore volume: 0.660 cm³/g)

Support 3:

natural silica (KA-1, produced by SUD-CHEMIE AG)
(specific surface area: 113 m²/g, pore volume: 0.64 cm³/g)

Support 4:

natural silica (KA-160, produced by SUD-CHEMIE AG)
(specific surface area: 130 m²/g, pore volume: 0.53
cm³/g)

Support 5:

synthetic silica (CARiACT Q-6, produced by Fuji
Silicia Kagaku K.K.) (specific surface area: 450 m²/g,
pore volume: 0.6 cm³/g)

Support 6:

synthetic silica (CARiACT Q-15, produced by Fuji
Silicia Kagaku K.K.) (specific surface area: 200 m²/g,
pore volume: 1.0 cm³/g)

Support 7:

synthetic silica (CARiACT Q-30, produced by Fuji
Silicia Kagaku K.K.) (specific surface area: 100 m²/g,
pore volume: 1.0 cm³/g)

Support 8:

synthetic silica (N-602A, produced by Nikki Kagaku
K.K.) (specific surface area: 290 m²/g, pore volume:
0.8 cm³/g)

Support 9:

synthetic silica (N-601A3, produced by Nikki Kagaku
K.K.) (specific surface area: 264 m²/g, pore volume:
0.9 cm³/g)

Support 10:

synthetic silica (N-602T, produced by Nikki Kagaku K.K.) (specific surface area: 132 m²/g, pore volume: 0.7 cm³/g)

[0084]

<Preparation Method of Catalyst 1>

The support 1 was dried for 4 hours in a (hot air) dryer previously adjusted to 110°C. 1 L of the previously dried carrier was subjected to the measurement of the bulk density by a 1 L-volume messcylinder. Tungstophosphoric acid and lithium nitrated were weighed each to the weight shown in Table 1, 15 ml of pure water was added thereto, and the mixture was uniformly dissolved to obtain a $\text{Li}_{0.1}\text{H}_{2.9}\text{PW}_{12}\text{O}_{40}$ aqueous solution (impregnating solution). This impregnating solution was allowed to rise in the cylinder with pure water to reach the liquid amount shown in the amount of prepared solution in Table 1 and then uniformly stirred. The previously dried support was weighed to the amount described in Table 1, added to the impregnating solution and thoroughly stirred, thereby impregnating the support. The support impregnated with the solution was air dried for 1 hour and thereafter dried for 5 hours by a hot air dryer adjusted to 150°C. The weight of the catalyst obtained was measured.

[0085]

<Preparation Method of Catalysts 2 to 12>

The preparation was performed by changing the kind and weight of the support, the kind and weight of the catalyst component and the weight of lithium nitrate as shown in Table 1 in Preparation Method of Catalyst 1. The bearing on the support was performed in the same manner as in Preparation Method of Catalyst 1.

[0086]

[Table 1]

Name of Catalyst	Support	Bulk Density (g/L)	Weight of Support (g)	Kind of Catalyst Component	Amount of Catalyst Component (g)	Amount of Lithium Nitrate (g)	Volume of Prepared Solution (ml)	Dry Weight (g)
catalyst 1	1	558	55.8	HPW	65.33	0.1318	34	113.6
catalyst 2	2	456	45.6	HSiW	34.88	0.0719	43	75.6
catalyst 3	3	573	57.3	HPW	65.33	0.1318	33	124.5
catalyst 4	4	575	57.5	HPW	65.33	0.1318	32	113.8
catalyst 5	5	627	62.7	HSiW	34.88	0.0719	33	94.3
catalyst 6	6	446	44.6	HSiW	34.88	0.0719	40	75.2
catalyst 7	7	432	43.2	HSiW	34.88	0.0719	41	74.5
catalyst 8	8	811	81.1	HPW	35.63	0.0718	64	114.7
catalyst 9	9	703	70.3	HPW	35.63	0.0718	83	102.9
catalyst 10	10	813	81.3	HPW	35.63	0.0718	69	114.3
catalyst 11	2	456	45.6	HPVW	35.90	0.0753	43	76.3
catalyst 12	2	456	45.6	HSiVW	35.90	0.0753	43	75.9

HPW: $H_3PW_{12}O_{40}$
 HSiW: $H_4SiW_{12}O_{40}$
 HPVW: $H_4PVW_{12}O_{40}$
 HSiVW: $H_5SiVW_{12}O_4$

[0087]

[Example 1]

40 ml of the catalyst obtained by Preparation Method of Catalyst 1 was filled in a reaction tube and a mixed gas of ethylene : acetic acid : steam : nitrogen shown in Table 2 was introduced thereinto at a temperature of 165°C and a pressure of 0.8 MPaG (gauge pressure) to perform the reaction. The results are shown in Table 3.

[0088]

[Table 2]

	Catalyst	Starting Material Gas, ethylene:acetic acid: water:nitrogen: substance added (molar ratio)	Substance Added (ppm)*1	Gas Flow Rate (NL/hr)	Pressure (MPaG)	Reaction Time (hr)	Reaction Temperature (°C)
Example 1	1	78.5:8.0:4.5:9.0	none	60.0	0.8	5 100	165
Example 2	2	78.5:8.0:4.5:9.0	none	60.0	0.8	5 99	165
Example 3	3	78.5:8.0:4.5:9.0	none	60.0	0.8	5 100	165
Example 4	4	78.5:8.0:4.5:9.0	none	60.0	0.8	5 103	165
Example 5	5	78.5:8.0:4.5:9.0	none	60.0	0.8	5 98	165
Example 6	6	78.5:8.0:4.5:9.0	none	60.0	0.8	5 100	165
Example 7	7	78.5:8.0:4.5:9.0	none	60.0	0.8	5 100	165
Example 8	8	78.5:8.0:4.5:9.0	none	60.0	0.8	5 100	165
Example 9	9	78.5:8.0:4.5:9.0	none	60.0	0.8	5 100	165
Example 10	10	78.5:8.0:4.5:9.0	none	60.0	0.8	5 100	165
Example 11	11	78.5:8.0:4.5:9.0	none	60.0	0.8	5 100	165

	Catalyst	Starting Material Gas, ethylene:acetic acid: water:nitrogen: substance added (molar ratio)	Substance Added (ppm)*1	Gas Flow Rate (NL/hr)	Pressure (MPaG)	Reaction Time (hr)	Reaction Temperature (°C)
Example 12	12	78.5:8.0:4.5:9.0	none	60.0	0.8	5 100	165
Comparative Example 1	1	78.5:8.0:4.5:8.2:0.8	1-butene (10088)	60.5	0.8	5 100	165
Comparative Example 2	1	78.5:8.0:4.5:8.2:0.8	2-octene (10088)	60.5	0.8	5 103	165
Comparative Example 3	1	78.5:8.0:4.5:8.2:0.8	TMP (10088)	60.5	0.8	5 98	165
Comparative Example 4	2	78.5:8.0:4.5:8.2:0.8	1-butene (19975)	60.5	0.8	5 102	165
Comparative Example 5	1	78.5:8.0:4.5:7.4:1.6	2-BA (19975)	61.0	0.8	5 105	165
Comparative Example 6	1	78.5:8.0:4.5:8.2:0.8	2-BuOH (19975)	61.0	0.8	5 98	165
Comparative Example 7	2	78.5:8.0:4.5:7.8:1.2	2-BEE (15056)	60.7	0.8	5 100	165

TMP: 2,2,4-trimethylolpentane

2-BEE: 2-butyl ethyl ether

2-BA: 2-butyl acetate

2-BuOH: 2-butyl alcohol

*1: concentration (ppm) when additive/(ethylene + substance added)

[0089]

[Table 3]

	Catalyst	Substance Added (ppm)*1	STY of Ethyl Acetate (g/L-hr)	Trace By- Products (wt%)
Example 1	1	none	191	0.0047
			186	0.0123
Example 2	2	none	252	0.0001
			236	0.0007
Example 3	3	none	212	0.0004
			204	0.0160
Example 4	4	none	224	0.0127
			213	0.0234
Example 5	5	none	268	0.0003
			251	0.0010
Example 6	6	none	189	0.0003
			180	0.0005
Example 7	7	none	130	0.0004
			125	0.0008
Example 8	8	none	178	0.0009
			169	0.0012
Example 9	9	none	95	0.0006
			90	0.0010
Example 10	10	none	205	0.0303
			185	0.0011
Example 11	11	none	148	0.0303
			140	0.0400
Example 12	12	none	139	0.0160
			131	0.0250

*1: concentration (ppm) when additive/(ethylene + substance added)

[0090]

[Examples 2 to 12]

The reactions were performed in the same manner as in Example 1 except for changing Catalyst 1 in Example 1 to Catalysts 2 to 12 as shown in Table 2. The results are shown in Table 3.

[0091]

[Comparative Examples 1, 2, 3, 5 and 6]

The reactions were performed in the same manner as in Example 1 except for changing the reaction gas composition as shown in Table 2. The results are shown in Table 4. As compared with Example 1, the STY of ethyl acetate after about 100 hours seriously decreased, trace by-products increased and a part was separated from the reaction solution and became oily.

[0092]

[Table 4]

	Catalyst	Substance Added (ppm)*1	STY of Ethyl Acetate (g/L-hr)	Trace By-Products (wt%)
Comparative Example 1	1	1-butene (10088)	200	2.4277
			166	5.3126
Comparative Example 2	1	2-octene (10088)	66	Oil was produced.
			43	Oil was produced.
Comparative Example 3	1	TMP (10088)	197	Oil was produced.
			171	Oil was produced.
Comparative Example 4	2	1-butene (19975)	203	6.3111
			165	8.2766
Comparative Example 5	1	2-BA (19975)	192	1.9833
			153	3.5211
Comparative Example 6	1	2-BuOH (19975)	195	1.5633
			177	3.0122
Comparative Example 7	2	2-BEE (15056)	203	6.3111
			181	7.2812

TMP: 2,2,4-trimethylolpentane

2-BEE: 2-butyl ethyl ether

2-BA: 2-butyl acetate

2-BuOH: 2-butyl alcohol

*1: concentration (ppm) when additive/(ethylene + substance added)

[0093]

[Comparative Examples 4 and 7]

The reactions were performed in the same manner as in Example 2 except for changing the reaction gas composition as shown in Table 2. The results are shown in Table 4. As compared with Example 2, the STY of ethyl acetate seriously decreased and trace by-products increased.

[0094]

[Example 13]

750 ml of the catalyst shown in Table 5 was filled in a reactor of a reaction apparatus schematically shown in Fig. 3. The conditions were set such that the temperature of the reactor was 160°C, the temperature of the vaporizer was 180°C, the pressure of the entire system was 0.8 MPaG (gauge pressure) and the condensation temperature in the scrubber was -5°C. The amount of ethylene fed in Fig. 3 was 49.0 g/hr and the gas not condensed in the scrubber was recycled by a compressor. Other conditions are shown in Table 5.

[0095]

[Table 5]

	Catalyst	Gas Composition in (l) after the reaction for 100 Hours, ethylene:acetic acid:water:nitrogen:ethyl acetate:butene (molar ratio)	Butene Concen- tration (ppm)	Gas Flow Rate (NL/hr)	Pressure (MPaG)	Temper- ature of Scrubber (°C)	Reaction Time (hr)	Reaction Temper- ature (°C)	STY of Ethyl Acetate (g/L-hr)	Trace By- Products (wt%)
Example 13	1	78.5:8.0:4.5:8.8:0.2:0.0016	20	1125	0.8	-5	100	165	181	0.0056
							500		183	
Example 14	2	78.5:8.0:4.5:8.7:0.2:0.0950	1200	1125	0.8	10	100	165	240	0.0005
							500		228	
Example 15	1	78.5:8.0:4.5:8.5:0.2:0.318	4000	1125	0.8	30	100	165	175	0.0086
							500		148	
Comparative Example 8	1	78.5:8.0:4.5:7.8:0.2:0.953	12000	1125	0.8	60	100	165	160	5.9030
							500		73	

[0096]

After starting the feeding of raw materials, the inlet concentration (analysis value at (1) of Fig. 3) was stabilized within 50 hours, therefore, the operation was continued as it is. The reaction results calculated from the inlet concentration and the reaction gas concentration at the outlet (analysis value at (3) of Fig. 3) after 100 hours or 500 hours are shown in Table 5.

[0097]

[Examples 14 and 15 and Comparative Example 8]

The reactions were performed in the same manner as in Example 13 except for changing the catalyst, the butene concentration and the temperature in the scrubber to the conditions shown in Table 5.

The reaction results are shown in Table 5.

[0098]

[Effects of the Invention]

As verified from the results in the foregoing pages, in the method for producing an ester from a carboxylic acid and an ethylene in the presence of an acid catalyst, when the concentration of an olefin having 3 or more carbon atoms in the raw materials is controlled to 10,000 ppm or less in terms of a molar ratio to the total of this substance and the ethylene or when the concentration of an equivalent of an olefin in the raw materials is controlled

to 50,000 ppm or less in terms of a molar ratio to the total of this substance and the ethylene, a stable operation can be continuously performed for a long period of time.

[0099]

[BRIEF DESCRIPTION OF DRAWINGS]

The figures are a view showing the process in one embodiment of the mode for carrying out the present invention and a schematic view of a testing apparatus used in the Examples.

[0100]

[Fig. 1]

Fig. 1 is a view showing a one-path process having no circulation step.

[Fig. 2]

Fig. 2 is a view showing a process having a circulation step from the post-step.

[Fig. 3]

Fig. 3 is a schematic view of a testing apparatus used in the Examples.

[NAME OF THE DOCUMENT] Abstract

[SUMMARY]

[PROBLEM TO BE SOLVED]

To provide a method for manufacturing an ester by esterifying a carboxylic acid with an ethylene, in which a stable operation can be continuously performed for a long period of time.

[MEANS TO SOLVE THE PROBLEM]

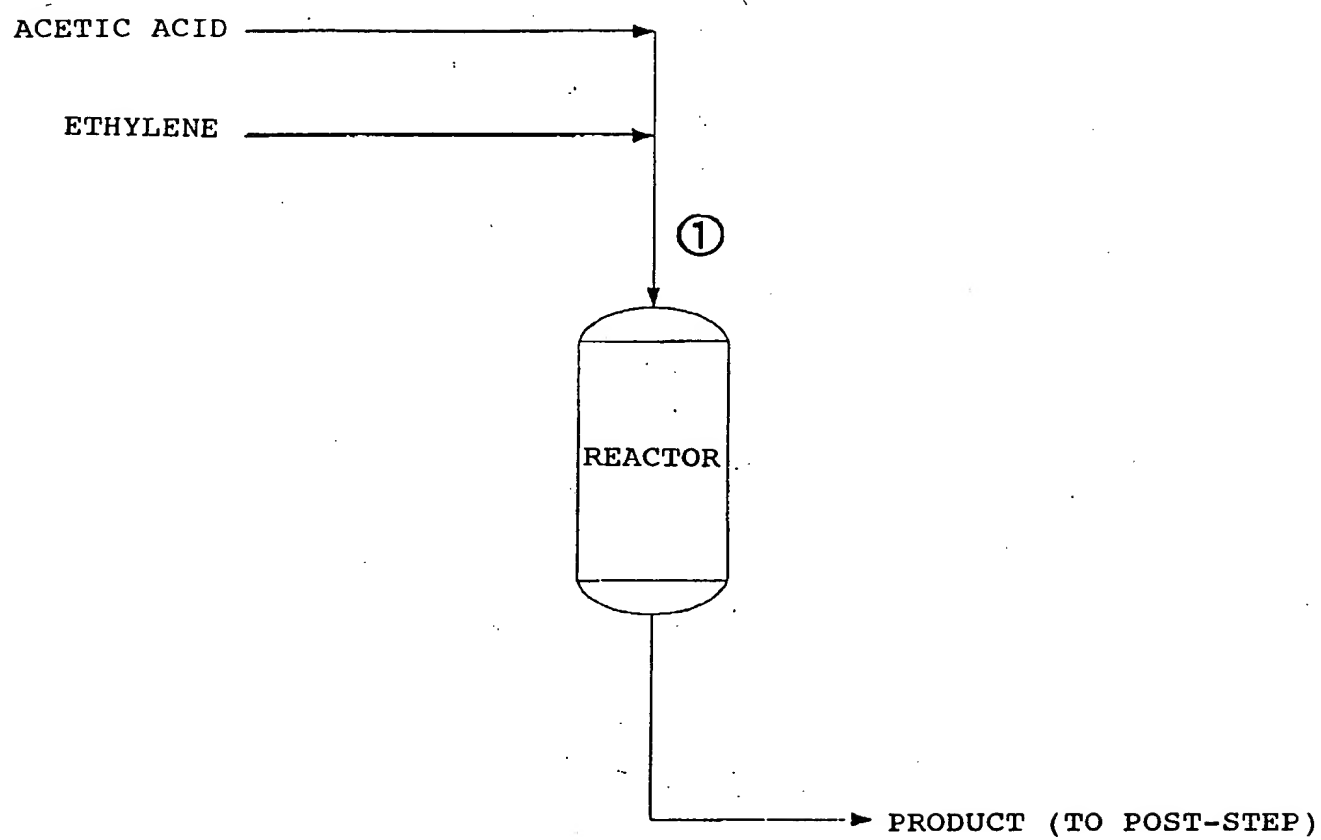
It has been found that in a method for manufacturing an ester by esterifying a carboxylic acid and an ethylene using an acid catalyst in a vapor phase, when the concentration of an olefin having 3 or more carbon atoms in the starting materials is controlled to 10,000 ppm or less in terms of the molar ratio to the total of this substance and the ethylene, the deterioration of the catalyst can be remarkably prevented from proceeding and in turn, a continuous and stable operation can be performed for a long time.

[SELECTED DRAWING] None.

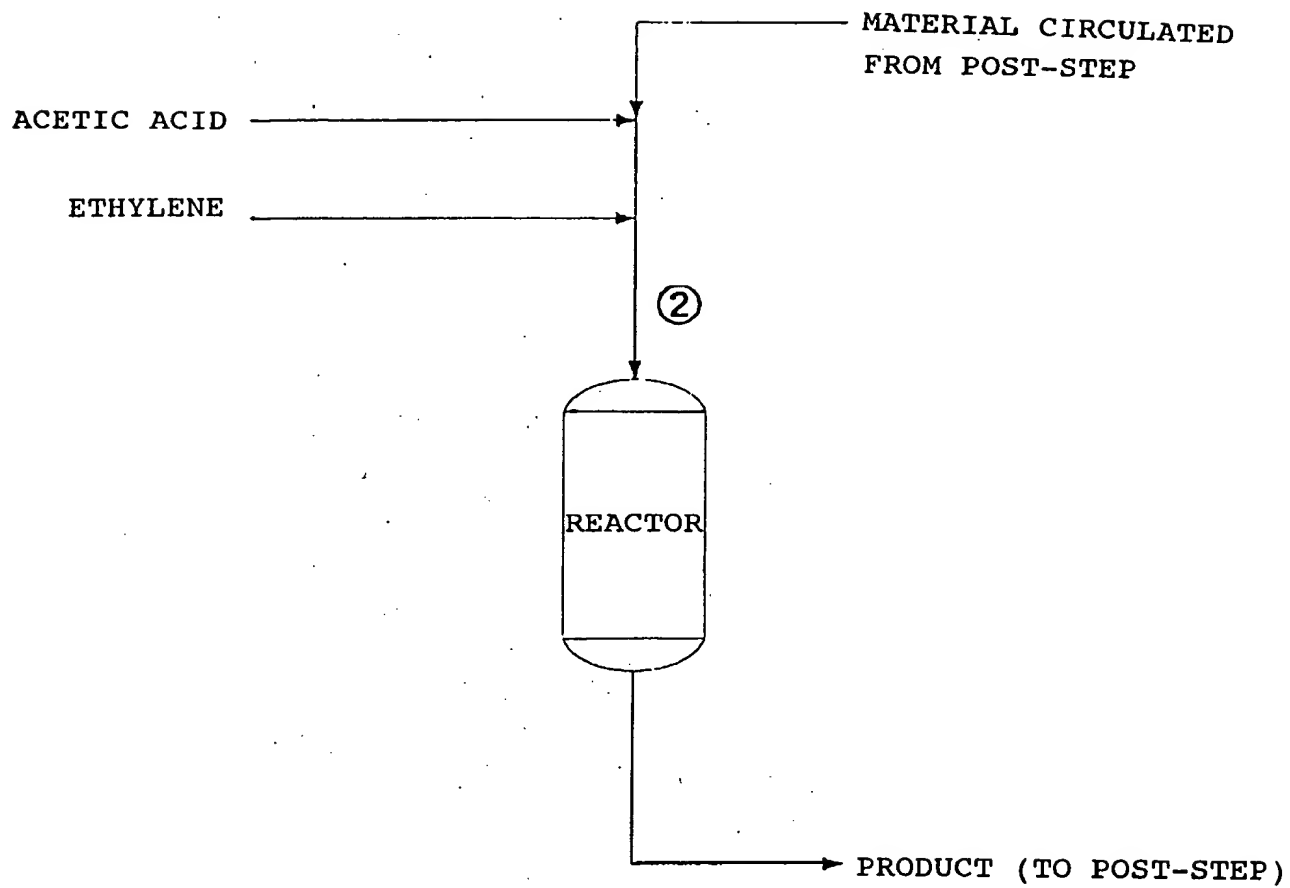
[NAME OF DOCUMENT]

Drawings

[FIG. 1]



[FIG. 2]



[FIG. 3]

